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# Iron(III) Metallacryptand and Metallacryptate Assemblies Derived from Aroylbis(*N*,*N*-diethylthioureas)

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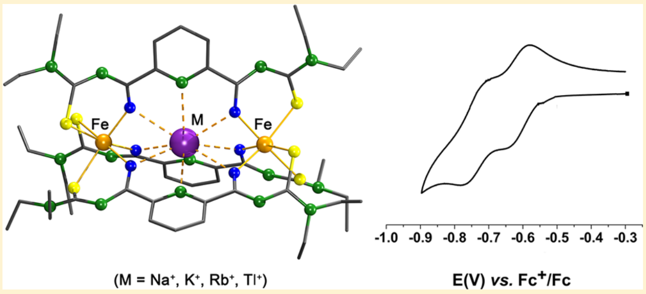
*Supporting Information*



**ABSTRACT:** The reaction of isophthaloylbis(*N*,*N*-diethylthiourea), $H_2L^1$, with $FeCl_3 \cdot 6H_2O$ gives the dinuclear tris-complex $[Fe_2(L^1)_3]$ (**5**), possessing a cryptand-like structure. A similar reaction with the ligand 2,6-dipicolinoylbis(*N*,*N*-diethylthiourea), $H_2L^2$, however, results in the formation of the anionic, mononuclear Fe(III) complex $[Fe(L^2)_2]^-$ (**6**), which could be isolated as its "$Tl^+$ salt" by the subsequent addition of $Tl(NO_3)$. A tighter view to the solid state structure of the obtained product, however, characterizes compound **6** as a one-dimensional coordination polymer, in which four-coordinate $Tl^+$ ions connect the $\{[Fe(L^2)_2]^-\}$ units to infinite chains. When $Fe^{3+}$ ions and $Tl^+$ ions are added to $H_2L^2$ simultaneously in a one-pot reaction, a different product is obtained: a cationic trinuclear complex of the composition $\{M\subset[Fe_2(L^2)_3]\}^+$. It has been isolated as a $PF_6^-$ salt and represents a {2}-metallacryptate with a nine-coordinate $Tl^+$ ion in the central void. Structurally related products of the compositions $\{M\subset[Fe_2(L^2)_3]\}(PF_6)$ ($M = Na^+, K^+, Rb^+$) (**8**($PF_6$)) could be isolated from analogous reactions with alkaline salts instead of $Tl(NO_3)$. {2}-Metallacryptates with larger central voids were synthesized with the ether-spaced aroylbis(*N*,*N*-diethylthiourea) $H_2L^3$. The compounds $\{M\subset[Fe_2(L^3)_3]\}(PF_6)$ ($M = K^+, Rb^+, Tl^+$ or $Cs^+$) (**9**($PF_6$)) were prepared by a similar protocol like those with $H_2L^2$ with the simultaneous addition of the metal ions to a solution of $H_2L^3$. Due to the larger spacer between the aroylthiourea units, the coordination number of the central $M^+$ ions is 12 by six carbonyl and six ether oxygen atoms. All products were characterized by elemental analysis, IR spectroscopy, and X-ray structure analysis. Cyclic voltammetric studies were carried out with the three representative complexes $[Fe_2(L^1)_3]$, $\{K\subset[Fe_2(L^2)_3]\}(PF_6)$, and $\{K\subset[Fe_2(L^3)_3]\}(PF_6)$. The obtained voltammograms indicate the dependence of the redox properties of the oligonuclear systems on the conjugation in the organic backbones of the ligands.

## ■ INTRODUCTION

Metallacryptands (**1**) and metallacryptates (**2**) belong to one of the most well-known classes of compounds, helicates, which have been extensively studied in metallo-supramolecular chemistry.[1−15] In addition to the topological analogy between the well-known cryptands and metallacryptands, these compounds have a number of advantages over their organic counterparts. Particularly, they are accessible in high yields in one-pot reactions and exhibit spectroscopic, electronic, and magnetic properties, which are inaccessible with their organic analogues.[16,17] Some strategies, namely, Raymond's symmetry-interaction method[18] and Saalfrank and Albrecht's template-directed approach,[19−22] have been developed and widely used for rational syntheses of aesthetic metallacryptands/metallacryptates.

Due to the strict requirements of chemical information being encoded in the subunits, however, the selection of appropriate building blocks continues to be a challenge in the designing of self-assembled metallacryptands. In this report, the potential exploitation of aroylbis(*N*,*N*-dialkylthioureas) as molecular components for the construction of such systems will be discussed.

*N*-Benzoyl(*N*′,*N*′-dialkylthioureas) are known as versatile ligands, which form stable complexes with a large number of transition metal ions.[23] In the majority of structurally characterized complexes, the ligands act as monoanionic, bidentate *S*,*O* chelators. Such a coordination mode also plays a vital role in binuclear complexes of the extended bipodal ligand isophthaloylbis(*N*,*N*-diethylthiourea) $H_2L^1$ with divalent transition metal ions such as $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Pd^{2+}$, or $Pt^{2+}$ (**3**),[24−26] but also with $In^{3+}$ (**4**) or the $\{ReO\}^{2+}$ or $\{Re_2O_3\}^{4+}$ cores.[27,28]

Recently, a number of heterometallic host−guest assemblies of different topologies have been reported with 2,6-dipicolinoylbis(*N*,*N*-diethylthiourea) $H_2L^2$, a ligand, which has the same molecular skeleton as $H_2L^1$, but with a central disubstituted pyridine ring instead of a phenylene ring.[29] This results in a completely different coordination chemistry. The

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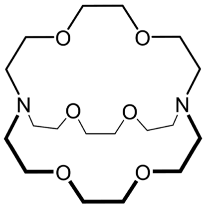
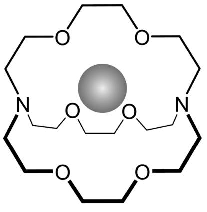
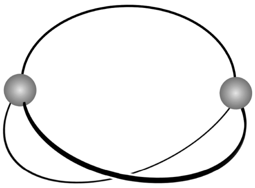


Cryptand



Cryptate



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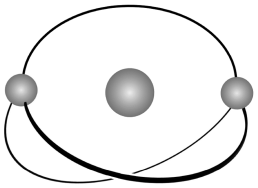

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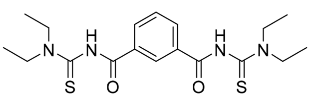
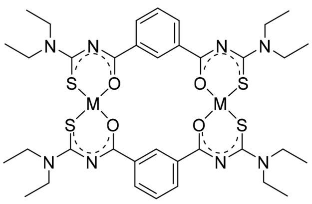


$H_2L^1$



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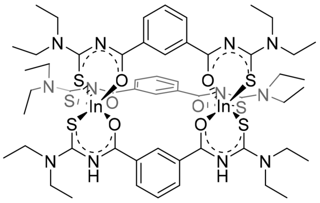

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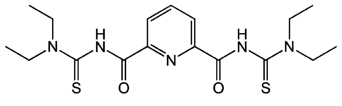
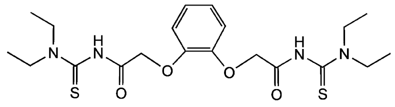
reported complexes were formed by self-assembly, but the obtained structural features can readily be understood following basic concepts of inorganic and coordination chemistry, such as Pearson's concept of hard and soft acids and bases,[13] the size or preferred coordination polyhedra of the used metal ions. Thus, "hard" and large metal ions, such as lanthanide or alkaline or alkaline earth ions, are preferably directed to the central void formed by two or three ligands $\{L^2\}^{2-}$, while octahedral transition metal ions coordinate to the *S*,*O* chelating units.[29] With regard to the obtained host−guest chemistry, it could be interesting to increase the central void further in order to host larger metal ions and/or to allow a controlled metal-exchange behavior in this position. A potentially suitable ligand is the novel catechol derivative $H_2L^3$, which not only increases the size of the central void but also provides more donor atoms for the coordination of large metal ions.



$H_2L^2$



$H_2L^3$

The present communication reports the coordination chemistry of Fe(III) ions with the ligands $H_2L^1$, $H_2L^2$, and $H_2L^3$ in combination with other metal ions such as alkaline metal ions or $Tl^+$.

## ■ EXPERIMENTAL SECTION

**Materials.** All chemicals used in this study were reagent grade and used without further purification. Solvents were dried and distilled. *N*,*N*-Diethylthiourea was synthesized following the procedure reported by Yokoyama et al.[30] The preparation of 2,2′-[1,2-phenylenebis(oxy)]diacetic acid was adopted from the literature.[31]

**Physical Measurements.** IR spectra were measured from KBr pellets on a Shimadzu FTIR 8300 spectrometer between 400 and 4000 $cm^{-1}$. NMR spectra were recorded on a JEOL 400 MHz spectrometer. ESI mass spectra were measured with an Agilent 6210 ESI-TOF (Agilent Technology) mass spectrometer. Elemental analyses of carbon, hydrogen, nitrogen, and sulfur were determined using a Heraeus vario EL elemental analyzer. Reproductions of the IR, NMR, and MS spectra are given as Supporting Information. Cyclic voltammetry was performed at room temperature at a platinum electrode in DMF solutions containing $(n\text{-}Bu_4N)(PF_6)$ (0.15 M) and the complex (0.2 mM), under an argon atmosphere. A three electrode setup with a Gamry PCI4/300 potentiostat board and the PHE200 software was used. Redox potentials were internally referenced against ferrocenium/ferrocence ($Fc^+$/Fc).

**Syntheses of the Ligands.** ***$H_2L^1$.*** The ligand was synthesized according to the method outlined by Douglas and Dains.[32] Yield: 70%. Elemental analysis calcd for $C_{18}H_{26}N_4O_2S_2$: C, 54.80; H, 6.64; N, 14.20; S, 16.25%. Found: C, 55.16; H, 6.38; N, 14.36; S, 15.96%. IR (KBr, $cm^{-1}$): 3119 (m), 2974 (m), 2938 (m), 2876 (m), 1690 (s), 1537 (s), 1449 (s), 1431 (s), 1281 (m), 1215 (s), 1130 (s), 1076 (m), 887 (w), 725 (m). $^1$H NMR (400 MHz, $CDCl_3$, ppm): 9.03 (s, 2H, NH); 8.25 (s, 1H, Ph), 7.97 (dd, *J* = 7.6 Hz, 1.6 Hz, 2H, Ph), 7.53 (t, *J* = 8.0 Hz, 1H, Ph); 4.01 (q, *J* = 7.0 Hz, 4H, $CH_2$); 3.59 (q, *J* = 7.0 Hz, 4H, $CH_2$), 1.35 (t, *J* = 7.2 Hz, 6H, $CH_3$); 1.30 (t, *J* = 7.2 Hz, 6H, $CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 179.5 (C═O); 163.6 (C═S); 133.0, 132.8, 129.5, 126.8 (Ph); 47.9, 47.6 ($CH_2$); 13.4, 11.5 ($CH_3$). ESI$^+$ MS (*m*/*z*): 811.2903 (calcd 811.2892), 81% $[2M + Na]^+$; 433.1138 (calcd 433.1134), 52% $[M + K]^+$; 417.1401 (calcd 417.1395), 100% $[M + Na]^+$; 395.1574 (calcd 395.1575), 10% $[M + H]^+$.

*$H_2L^2$.* The synthesis of $H_2L^2$ was performed by the procedure published by Dixon and Taylor with some modifications.[33] A mixture of previously dried dipicolinic acid (3.34 g, 0.02 mol), $SOCl_2$ (30 mL, 0.4 mol), and a few drops of DMF was heated on reflux under an argon atmosphere until a clear solution was obtained. Subsequently, the reaction mixture was stirred for two more hours and the residual $SOCl_2$ was removed under reduced pressure. This gives a colorless solid of dipicolinoyl dichloride. This solid was dissolved in dry THF (60 mL) and added dropwise at 0 °C (ice bath) to a mixture of *N*,*N*-diethylthiourea (5.28 g, 0.04 mol) and $Et_3N$ (8.5 mL, 0.06 mol) in dry THF (30 mL) under an argon atmosphere. The resulting mixture was warmed up to 40−50 °C and stirred for 2 h. After cooling to room temperature, the formed colorless precipitate of $(Et_3NH)Cl$ was filtered off and the THF was removed under reduced pressure. The resulting solid was washed thoroughly with MeOH, which finally gave the ligand $H_2L^2$ as a colorless solid. Yield: 92% (7.27 g). Elemental analysis calcd for $C_{17}H_{25}N_5O_2S_2$: C, 51.62; H, 6.37; N, 17.71; S, 16.21%. Found: C, 51.70; H, 6.29; N, 17.79; S, 15.79%. IR (KBr, $cm^{-1}$): 3267 (m), 2974 (w), 2934 (w), 2874 (w), 1674 (s), 1520 (s), 1449 (s), 1418 (s), 1277 (m), 1225 (s), 1101 (w), 997 (w), 752 (m). $^1$H NMR (400 MHz, $CDCl_3$, ppm): 9.82 (s, 2H, NH); 8.41 (d, *J* = 8.0 Hz, 2H, *m*-Py), 8.10 (t, *J* = 8.0 Hz, 1H, *p*-Py), 4.04 (q, br, *J* = 6.4 Hz, 4H, $CH_2$); 3.67 (q, br, *J* = 6.4 Hz, 4H, $CH_2$); 1.35 (s, br, 12H, $CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 178.3 (C═O); 159.3 (C═S); 148.0, 139.8, 126.9 (Py); 47.8, ($CH_2$); 13.6, 11.5 ($CH_3$). ESI$^+$ MS (*m*/*z*): 813.2796 (calcd 813.2797), 85% $[2M + Na]^+$; 434.1085 (calcd 434.1087), 10% $[M + K]^+$; 418.1349 (calcd 418.1347), 100% $[M + Na]^+$.

*$H_2L^3$.* The ligand $H_2L^3$ was prepared by a similar procedure as described for $H_2L^2$. A mixture of the dry dicarboxylic acid (4.52 g, 0.02

mol) prepared from catechol and two equivalents of chloroacetic acid and an excess of $SOCl_2$ (30 mL, 0.4 mol) was heated to reflux under an argon atmosphere for 3 h until a clear solution was obtained. The resulting reaction mixture was stirred for 2 more hours, and the residual $SOCl_2$ was removed under reduced pressure. The remaining solid was dissolved in dry THF (60 mL) and added dropwise at 0 °C (ice bath) under an argon atmosphere to a mixture of *N*,*N*-diethylthiourea (5.28 g, 0.04 mol) and $Et_3N$ (12.8 mL, 0.04 mol) in dry THF (30 mL). After warming to 40−50 °C and stirring for 2 h, the mixture was cooled to room temperature. A colorless precipitate of $(Et_3NH)Cl$ was filtered off, and THF was removed under reduced pressure. The resulting solid was washed thoroughly with MeOH to give the ligand $H_2L^3$ as a colorless solid. Yield: 70% (6.36 g). Elemental analysis calcd for $C_{20}H_{30}N_4O_4S_2$: C, 52.84; H, 6.65; N, 12.32; S, 14.11%. Found: C, 52.72; H, 6.81; N, 12.05; S, 13.94%. IR (KBr, $cm^{-1}$): 3154 (m), 2982 (w), 2938 (w), 1667 (s), 1528 (s), 1456 (m), 1427 (m), 1279 (m), 1234 (s), 1200 (s), 1142 (m), 1061 (w), 961 (w), 754 (m). $^1H$ NMR (400 MHz, $CDCl_3$, ppm): 8.92 (s, 2H, NH); 7.06−7.01 (m, 2H, Ph); 6.98−6.93 (m, 2H, Ph); 4.66 (s, 4H, $OCH_2$); 3.95 (q, *J* = 6.4 Hz, 4H, $NCH_2$); 3.55 (q, *J* = 6.4 Hz, 4H, $NCH_2$); 1.31 (t, *J* = 6.4 Hz, 6H, $CH_3$), 1.23 (t, *J* = 6.8 Hz, 6H, $CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 177.8 (C=O); 165.1 (C=S); 147.5, 123.7, 115.5 (Ph); 69.4 ($OCH_2$); 47.8 ($NCH_2$); 13.6, 11.5 ($CH_3$). $ESI^+$ MS (*m*/*z*): 931.3332 (calcd 931.3315), 85% $[2M + Na]^+$; 493.1349 (calcd 493.1345), 10% $[M + K]^+$; 477.1617 (calcd 477.1606), 100% $[M + Na]^+$; 455.1796 (calcd 455.1787), 5% $[M + H]^+$.

**Syntheses of the Complexes.** *$[Fe_2(L^1)_3]$*. $H_2L^1$ (59.2 mg, 0.15 mmol) was added to a solution of $FeCl_3\cdot 6H_2O$ (27.0 mg, 0.1 mmol) in 1 mL of MeOH. The ligand dissolved quickly, and a dark red precipitate deposited immediately from the solution after the addition of 2 drops of $Et_3N$. After stirring for 2 h at 50 °C, the product was filtered off, washed with a small amount of MeOH, and dried in vacuum. Single crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of the complex in DMF. Yield: 82% (53 mg). Elemental analysis calcd for $C_{54}H_{72}O_6N_{12}S_6Fe_2$: C, 50.30; H, 5.63; N, 13.04; S, 14.92%. Found: C, 50.15; H, 5.54; N, 13.09; S, 14.60%. IR (KBr, $cm^{-1}$): 3429 (w), 2976 (w), 2932 (w), 2870 (w), 1504 (s), 1422 (vs), 1354 (m), 1256 (w), 1076 (w), 725 (w). $ESI^+$ MS (*m*/*z*): 1327.2321 (calcd 1327.2358), 12% $[M + K]^+$; 1311.2590 (calcd 1311.2619), 33% $[M + Na]^+$; 1289.2771 (calcd 1289.2799), 30% $[M + H]^+$.

*$Tl[Fe(L^2)_2]$*. $H_2L^2$ (79.0 mg, 0.2 mmol) was added to a solution of $Fe(NO_3)_3\cdot 9H_2O$ (40.4 mg, 0.1 mmol) in 1.5 mL of MeOH. The color of the solution changed immediately to dark red. After stirring for 30 min at room temperature, 2 drops of $Et_3N$ and then $TlNO_3$ (26.6 mg, 0.1 mmol) dissolved in $H_2O$ (0.5 mL) were added to the reaction mixture. The temperature was increased to 50 °C and kept for 2 h. Slow evaporation of the solvent at room temperature resulted in precipitation of dark-red crystals, which were suitable for X-ray analysis. The product was filtered off, washed with cold MeOH, and dried in vacuum. Yield: 62% (65 mg). Elemental analysis calcd for $Tl[Fe(L^2)_2]\cdot H_2O$, $C_{34}H_{48}O_5N_{10}S_4FeTl$: C, 38.33; H, 4.54; N, 13.15; S, 12.04%. Found: C, 38.12; H, 4.42; N, 12.93; S, 11.80%. IR (KBr, $cm^{-1}$): 3422 (w), 2972 (w), 2932 (w), 2872 (w), 1601 (vs), 1499 (s), 1427 (s), 1360 (s), 1250 (s), 1099 (w), 957 (w), 756 (w). $ESI^-$ MS (*m*/*z*): 842.1966 (calcd 842.1936), 6% $[Fe(L^2)_2]^-$, 416.1231 (calcd 416.1191), 25% $[Na(L^2)]^-$.

*$\{M\subset[Fe_2(L^2)_3]\}(PF_6)$ ($M = Rb^+, K^+, Na^+, Tl^+$)*. $H_2L^2$ (59.3 mg, 0.15 mmol) was added to a solution of $FeCl_3\cdot 6H_2O$ (27.0 mg, 0.1 mmol) and 0.05 mmol of MCl ($M = Rb^+$, $K^+$, or $Na^+$) in 1 mL of MeOH and a few drops of $H_2O$ were added. Due to the low solubility of TlCl in $H_2O$ and MeOH in the case of $Tl^+$, the nitrate salts, $Fe(NO_3)_3\cdot 9H_2O$ and $TlNO_3$, were used. The ligand dissolved rapidly, and the color of the solution changed immediately to dark. The mixture was stirred for 30 min at room temperature, and 3 drops of $Et_3N$ were added. After stirring for additional 30 min, $(n\text{-}Bu_4N)(PF_6)$ (19.4 mg, 0.05 mmol) was added, and the temperature was increased to 50 °C and kept for 2 h. During this time, a dark precipitate deposited. The product was filtered off, washed with a small amount of MeOH, and dried in vacuum. Single crystals suitable for X-ray analysis were obtained by slow evaporation of solutions of the complexes in $CH_2Cl_2$/MeOH mixtures.

*$\{Rb\subset[Fe_2(L^2)_3]\}(PF_6)$*. Yield: 67% (49 mg). Elemental analysis calcd for $C_{51}H_{69}O_6N_{15}S_6PF_6Fe_2Rb$: C, 40.23; H, 4.57; N, 13.80; S, 12.63%. Found: C, 40.54; H, 4.62; N, 13.48; S, 12.87%. IR (KBr, $cm^{-1}$): 3427 (w), 2976 (w), 2934 (w), 1510 (s), 1433 (s), 1412 (s), 1356 (m), 1252 (m), 1150 (w), 839 (s), 746 (w), 557 (w). $ESI^+$ MS (*m*/*z*): 1376.1625 (calcd 1376.1696), 39% $\{Rb\subset[Fe_2(L^2)_3]\}^+$; 1330.2156 (calcd 1330.2215), 100% $\{K\subset[Fe_2(L^2)_3]\}^+$.

*$\{K\subset[Fe_2(L^2)_3]\}(PF_6)$*. Yield: 75% (65 mg). Elemental analysis calcd for $C_{51}H_{69}O_6N_{15}S_6PF_6Fe_2K$: C, 41.49; H, 4.71; N, 14.23; S, 13.03%. Found: C, 41.52; H, 4.65; N, 14.25; S, 13.18%. IR (KBr, $cm^{-1}$): 3441 (w), 2974 (w), 2934 (w), 1506 (s), 1435 (s), 1355 (m), 1254 (m), 1196 (w), 1076 (w), 841 (m). $ESI^+$ MS (*m*/*z*): 1330.2180 (calcd 1330.2215), 100% $\{K\subset[Fe_2(L^2)_3]\}^+$.

*$\{Na\subset[Fe_2(L^2)_3]\}(PF_6)$*. Yield: 90% (67 mg). Elemental analysis calcd for $C_{51}H_{69}O_6N_{15}S_6PF_6Fe_2Na$: C, 41.95; H, 4.76; N, 14.39; S, 13.18%. Found: C, 41.72; H, 4.53; N, 14.14; S, 13.42%. IR (KBr, $cm^{-1}$): 2974 (w), 2936 (w), 1541 (m), 1506 (s), 1437 (s), 1417 (s), 1355 (m), 1256 (m), 1152 (w), 1076 (w), 839 (m). $ESI^+$ MS (*m*/*z*): 1330.2172 (calcd 1330.2215), 100% $\{K\subset[Fe_2(L^2)_3]\}^+$; 1314.2408 (calcd 1314.2476), 13% $\{Na\subset[Fe_2(L^2)_3]\}^+$.

*$\{Tl\subset[Fe_2(L^2)_3]\}(PF_6)$*. Yield: 56% (46 mg). Elemental analysis calcd for $\{Tl\subset[Fe_2(L^2)_3]\}(PF_6)\cdot 3H_2O$, $C_{51}H_{75}O_9N_{15}S_6PF_6Fe_2Tl$: C, 36.13; H, 4.46; N, 12.39; S, 11.34%. Found: C, 35.95; H, 4.37; N, 12.07; S, 11.62%. IR (KBr, $cm^{-1}$): 3431 (w), 2976 (w), 2935 (w), 2872 (w), 1508 (s), 1431 (s), 1410 (s), 1356 (m), 1252 (m), 1150 (w), 839 (s), 746 (w), 557 (w). $ESI^+$ MS (*m*/*z*): 1330.2259 (calcd 1330.2215), 100% $\{K\subset[Fe_2(L^2)_3]\}^+$.

*$\{M\subset[Fe_2(L^3)_3]\}(PF_6)$ ($M = Cs^+, Rb^+, K^+, Tl^+$)*. $H_2L^3$ (68.2 mg, 0.15 mmol) was added to a solution of $FeCl_3\cdot 6H_2O$ (27.0 mg, 0.1 mmol) and 0.05 mmol of MCl ($M = Cs^+$, $Rb^+$ or $K^+$) in 1 mL of MeOH and a few drops of water. In the case of the $Tl^+$ complex, $Fe(NO_3)_3\cdot 9H_2O$ and $TlNO_3$ were used as starting materials. The ligand dissolved quickly, and the color of the solution changed immediately to dark red. The mixture was stirred at room temperature for 30 min, and 3 drops of $Et_3N$ were added. After stirring at room temperature for an additional 30 min, $(n\text{-}Bu_4N)(PF_6)$ (19.4 mg, 0.05 mmol) was added and the temperature was increased to 50 °C and kept for 2 h. During this process, a dark red precipitate deposited. The product was filtered off, washed with a small amount of MeOH, and dried in vacuum. Single crystals suitable for X-ray analysis were obtained by slow evaporation of solutions of the complexes in $CH_2Cl_2$/MeOH mixtures.

*$\{Cs\subset[Fe_2(L^3)_3]\}(PF_6)$*. Yield: 85% (74 mg). Elemental analysis calcd for $C_{60}H_{84}O_{12}N_{12}S_6PF_6Fe_2Cs$: C, 41.24; H, 4.85; N, 9.62; S, 11.01%. Found: C, 40.94; H, 4.62; N, 9.37; S, 10.87%. IR (KBr, $cm^{-1}$): 3427 (w), 2980 (w), 2936 (w), 1560 (m), 1533 (m), 1506 (vs), 1425 (vs), 1344 (m), 1248 (m), 1200 (m), 1126 (m), 841 (s), 745 (w), 557 (w). $ESI^+$ MS (*m*/*z*): 1601.2424 (calcd 1601.2409), 100% $\{Cs\subset[Fe_2(L^3)_3]\}^+$; 1507.2968 (calcd 1507.2992), 16% $\{K\subset[Fe_2(L^3)_3]\}^+$.

*$\{Rb\subset[Fe_2(L^3)_3]\}(PF_6)$*. Yield: 88% (75 mg). Elemental analysis calcd for $C_{60}H_{84}O_{12}N_{12}S_6PF_6Fe_2Rb$: C, 42.39; H, 4.98; N, 9.89; S, 11.32%. Found: C, 42.42; H, 4.97; N, 9.75; S, 11.46%. IR (KBr, $cm^{-1}$): 3441 (w), 2978 (w), 2932 (w), 1558 (m), 1539 (m), 1504 (vs), 1427 (vs), 1346 (m), 1254 (m), 1200 (w), 1126 (m), 841 (s), 744 (w), 559 (w). $ESI^+$ MS (*m*/*z*): 1553.2511 (calcd 1553.2473), 100% $\{Rb\subset[Fe_2(L^3)_3]\}^+$; 1507.2972 (calcd 1507.2992), 13% $\{K\subset[Fe_2(L^3)_3]\}^+$.

*$\{K\subset[Fe_2(L^3)_3]\}(PF_6)$*. Yield: 81% (65 mg). Elemental analysis calcd for $C_{60}H_{84}O_{12}N_{12}S_6PF_6Fe_2K$: C, 43.58; H, 5.12; N, 10.17; S, 11.64%. Found: C, 43.58; H, 5.46; N, 10.05; S, 11.64%. IR (KBr, $cm^{-1}$): 3429 (w), 2978 (w), 2932 (w), 1558 (m), 1539 (m), 1504 (vs), 1427 (vs), 1346 (m), 1254 (m), 1196 (w), 1126 (m), 841 (s), 741 (w), 559 (w). $ESI^+$ MS (*m*/*z*): 1507.3000 (calcd 1507.2992), 100% $\{K\subset[Fe_2(L^3)_3]\}^+$.

*$\{Tl\subset[Fe_2(L^3)_3]\}(PF_6)$*. Yield: 59% (54 mg). Elemental analysis calcd for $C_{60}H_{84}O_{12}N_{12}S_6PF_6Fe_2Tl$: C, 39.62; H, 4.66; N, 9.24; S, 10.58%. Found: C, 39.82; H, 4.73; N, 9.28; S, 10.17%. IR (KBr, $cm^{-1}$): 2978

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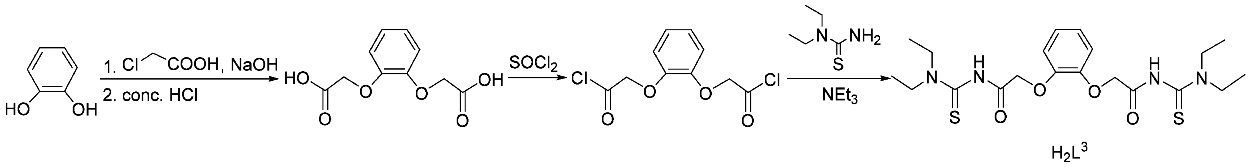
**Scheme 1. Synthesis of the Ether-Spaced Ligand $H_2L^3$**



(w), 2936 (w), 1557 (s), 1506, 1425 (s), 1342 (m), 1254 (m), 1198 (m), 1125 (m), 841 (s), 745 (w), 557 (w). ESI$^+$ MS ($m/z$): 1673.3220 (calcd 1673.3100), 84% $\{Tl\subset[Fe_2(L^3)_3]\}^+$; 1507.3108 (calcd 1507.2992), 100% $\{K\subset[Fe_2(L^3)_3]\}^+$.

**X-ray Crystallography.** The intensities for the X-ray determinations of $[TlFe(L^2)_2]\cdot0.5CH_2Cl_2$, $\{Rb\subset[Fe_2(L^2)_3]\}(PF_6)\cdot0.5CH_2Cl_2$, $\{K\subset[Fe_2(L^2)_3]\}(PF_6)\cdot0.5CH_2Cl_2$, $\{Cs\subset[Fe_2(L^3)_3]\}(PF_6)$, $\{Rb\subset[Fe_2(L^3)_3]\}(PF_6)$, $\{K\subset[Fe_2(L^3)_3]\}(PF_6)$, and $\{Tl\subset[Fe_2(L^3)_3]\}(PF_6)$ were collected on a STOE IPDS 2T instrument at 200 K with Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) using a graphite monochromator. The intensities for the X-ray determinations of $[Fe_2(L^1)_3]$, $\{Na\subset[Fe_2(L^2)_3]\}(PF_6)\cdot CH_2Cl_2$, and $\{Tl\subset[Fe_2(L^2)_3]\}(PF_6)\cdot CH_2Cl_2$ were collected on a Bruker D8 Venture instrument at 100 K with Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) using a TRIUMPH monochromator. Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with the SHELXS 97, SHELXS 86, and SHELXL 2014/7 programs included in the WinGX program package.[34−36] Hydrogen atoms were calculated for idealized positions and treated with the "riding model" option of SHELXL. Crystal data and structure determination parameters are given in Table S2.1. Additional information on the structure determinations has been deposited with the Cambridge Crystallographic Data Centre.

## ■ RESULTS AND DISCUSSION

Three aroylbis(*N*,*N*-dialkylthiourea) ligands, namely, isophthaloylbis(*N*,*N*-diethylthiourea) $H_2L^1$, 2,6-dipicolinoylbis(*N*,*N*-diethylthiourea) $H_2L^2$, and the novel ether-spaced $H_2L^3$, have been used for the syntheses of binuclear iron complexes. Syntheses and characterization of the ligands $H_2L^1$ and $H_2L^2$ have been reported previously.[28,33] The synthesis of $H_2L^3$ starts with the preparation of a dicarboxylic acid derived from catechol.[31] Then, this acid is converted into its dichloride by being refluxed in an excess of $SOCl_2$. The reaction of the dichloride with *N*,*N*-diethylthiourea in the presence of $Et_3N$ gives the ligand $H_2L^3$ in 70% yield (Scheme 1).

The IR spectrum of $H_2L^3$ is characterized by a medium broad absorption at 3163 cm$^{-1}$ and a strong absorption at 1659 cm$^{-1}$, which can be assigned to the stretching vibrations of the NH and C═O groups, respectively. The $^1$H NMR spectrum of $H_2L^3$ in $CDCl_3$ presents a broad signal at 8.92 ppm, which confirms the presence of NH protons. Another broad signal at 4.66 ppm is assigned to the methylene protons of $OCH_2$. Two well-separated signal sets of two ethyl groups indicate the hindered rotation around the C(S)−$NEt_2$ bond, which is normally observed for other aroyl-*N*,*N*-dialkylthioureas.[23−29]

When the ligand $H_2L^1$ reacts with iron(III) chloride in MeOH, after the addition of the supporting base $Et_3N$, a pure product with the composition of $[Fe_2(L^1)_3]$ deposits directly from the reaction mixture as a dark-red solid. In the IR spectrum of the compound, no absorptions in the region above 3100 cm$^{-1}$ corresponding to $\nu_{NH}$ stretches are observed. This is a sign of the deprotonation of the ligand during complexation. A bathochromic shift of the $\nu_{C=O}$ band from 1690 cm$^{-1}$ in $H_2L^1$ to 1504 cm$^{-1}$ in the complex strongly reflects the formation of *S*,*O* chelates. The result of the elemental analysis and the detection of the expected molecular ions as well as corresponding $[M + Na]^+$ and $[M + K]^+$ ions in the ESI$^+$ MS spectrum are clear evidence for the formation of a neutral complex with the composition of $[Fe_2(L^1)_3]$. This is confirmed by an X-ray diffraction analysis of single crystals obtained from slow evaporation of a solution of the complex in DMF. Figure 1 depicts the molecular structure of the compound. Selected bond lengths and torsion angles are given in Table S2.2.

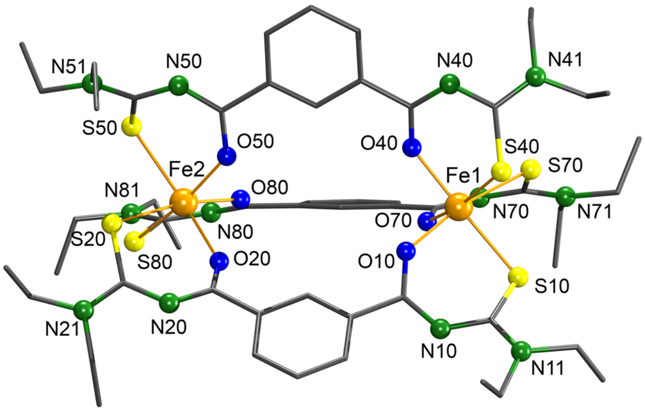
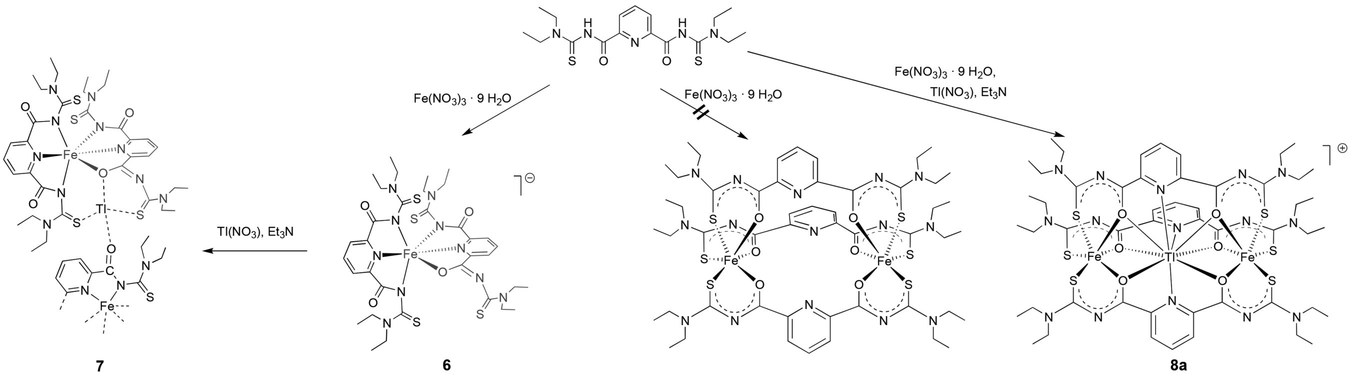


**Figure 1.** Molecular structure of $[Fe_2(L^1)_3]$ (**5**). Hydrogen atoms were omitted for clarity.

The coordination environments of the metal ions are similar to those in the In(III) complex, which has been recently reported.[27] In particular, the two iron ions coordinate with three bis(bidentate) deprotonated ligands $(L^1)^{2-}$ in distorted octahedral coordination modes with a facial arrangement of the donor atoms. The Fe−O and Fe−S bond lengths are in the same ranges as those recently reported for an Fe(III) complex of the simple bidentate benzoyl-*N*,*N*-diethylthiourea ligand.[37] Despite considerable deviation of the six-membered chelate rings from planarity, which is evident from the O−C−N−C and C−N−C−S torsion angles (Table S2.2), the typical extended $\pi$-systems for chelating aroylthiourea moieties are indicated by partial double bond character of the C−O, C−N, and C−S bonds.[29] Additionally, slightly longer C(S)−$N_{amide}$ bonds in comparison with the adjacent C(O)−$N_{amide}$ bonds illustrate that electron density of the *S*,*O* chelates locates less on the "soft" S donors than on the "hard" O donors, which are in favor of the "hard" acceptor Fe$^{3+}$. With its empty void, the cryptand-like metallacycle $[Fe_2(L^1)_3]$ could be suitable as hosts for metal ions. However, all attempts to produce such inclusion complexes with small cations, even with Li$^+$, have failed. This result is probably due to the fact that the coordination capacity of the central void is insufficient for cation binding, and more seriously, the direction of three inner hydrogen atoms of the phenylene spacers pointing toward the centers of the cavities remarkably reduces their effective size. These complications will be overcome, when the internal phenylene C−H group of $H_2L^1$ is replaced by a pyridine N atom as being done with the synthesis of $H_2L^2$.

**Scheme 2. Synthesis of the Fe/Tl Mixed-Metal Complexes with the Ligand $H_2L^2$**



Assuming that the *S,O* coordination mode of the ligand remains after the modification of the spacer, a neutral {2}-metallacryptand with the composition of $[Fe_2(L^2)_3]$ should result from the reaction of $Fe^{3+}$ ions and $H_2L^2$ under the same conditions used for the synthesis of the previous complex. But all our attempts to isolate such a neutral iron(III) cryptand failed. The formed dark red complex was very well soluble in MeOH, which is a strong indicator for the formation of an ionic compound. After efforts to precipitate such species with different counterions, finally a crystalline product was isolated after the addition of Tl(I) ions with a yield of 62%. The IR spectrum of the compound exhibits a strong $\nu_{C=O}$ band at 1601 $cm^{-1}$, which corresponds to a bathochromic shift of approximately 70 $cm^{-1}$ with respect to the uncoordinated ligand. Compared to the standard value of approximately 200 $cm^{-1}$ reported for benzoylthioureato chelates,[27,28,37] the shift is quite moderate and might be caused by a smaller degree of electron delocalization within the aroylthiourea moieties. The absence of a $\nu_{NH}$ band in the region above 3100 $cm^{-1}$ indicates the expected deprotonation of the ligand. Slow evaporation of the solution of the product in a $CH_2Cl_2$/MeOH mixture gave single crystals of good quality. An X-ray diffraction analysis exhibits a structure against the expectation of the neutral {2}-metallacryptand $[Fe_2(L^2)_3]$. The composition of the unexpected compound can be described as an ion pair between $[Fe(L^2)_2]^-$ anions (**6**) and $Tl^+$ cations or the $[TlFe(L^2)_2]_\infty$ polymer (**7**) (Scheme 2). It is supported by elemental analysis and the presence of a peak associated with the fragment $[Fe(L^2)_2]^-$ in the $ESI^-$ MS spectrum. Figure 2a illustrates the structure of the unusual mixed-metal complex. Selected bond lengths are summarized in Table 1.

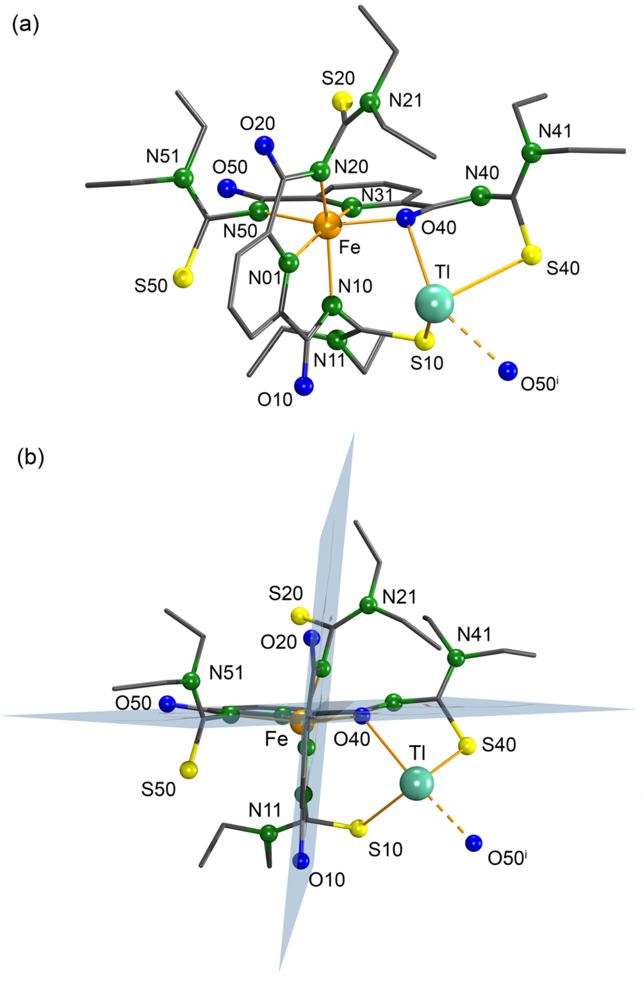


**Figure 2.** (a) Molecular structure of $[TlFe_2(L^2)_2]_\infty$ (**7**). (b) View along the N01−Fe−N31 connecting line. Hydrogen atoms were omitted for clarity.

The $Fe^{3+}$ ion is six-coordinate with a distorted octahedral environment formed by two planar donor atom sets, (*N,N,N*) and (*O,N,N*). Each of them belongs to one doubly deprotonated pincer ligand $(L^2)^{2-}$. The former donor sets consist of the pyridine N atom and two amide N atoms of the first and second aroyl thiourea arms. Such a coordination mode is found in the dinuclear Ni(II) complex of the ligand $H_2L^2$,[29] and it is commonly observed in several bis-chelates of pincer-type ligands based on pyridine-2,6-dicarboxamide.[38−41] The latter donor sets comprise the pyridine N atom of the other ligand, the carbonyl O atom of its first arm, and the amide N atom of the second arm. The fact that the C−O and C−S bonds in the amide-coordinated arms are shorter than those in the chelate rings of $[Fe_2(L^1)_3]$ implies the greater double bond character of these bonds and, thus, the location of the negative charge of the arms on the amide N atoms, which directly bind to the $Fe^{3+}$ ion. A similar charge location on the O40 atom can be deduced from the remarkably elongated C40−O40 bond and the shortened C40−N40 bond. The resulting hard Lewis base $\{O40\}^-$ acts as a bridging ligand between the "hard" Lewis acids $Fe^{3+}$ and $Tl^+$.

The $Tl^+$ ions connect the "$[Fe(L^2)_2]^-$ anions" to 1D polymers by establishing long-range bonds to two sulfur atoms and the oxygen atom O40 and an oxygen atom of an adjacent unit. The resulting coordination polyhedron of thallium can be best described as a square pyramid or a distorted pseudo-

Table 1. Selected Bond Lengths (Å) in $[TlFe(L^2)_2]_\infty$

| | | | | | |
|---|---|---|---|---|---|
| Fe–N01 | 2.117(5) | O10–C10 | 1.228(9) | O40–C40 | 1.302(7) |
| Fe–N10 | 2.139(5) | C10–N10 | 1.356(8) | C40–N40 | 1.292(8) |
| Fe–N20 | 2.064(6) | N10–C11 | 1.413(8) | N40–C41 | 1.384(9) |
| Fe–N31 | 2.074(5) | C11–N11 | 1.308(9) | C41–N41 | 1.323(1) |
| Fe–O40 | 2.048(4) | C11–S10 | 1.701(7) | C41–S40 | 1.698(8) |
| Fe–N50 | 2.132(5) | O20–C20 | 1.245(8) | O50–C50 | 1.236(8) |
| Tl–S10 | 3.004(2) | C20–N20 | 1.341(8) | C50–N50 | 1.344(8) |
| Tl–S40 | 2.967(2) | N20–C21 | 1.415(9) | N50–C51 | 1.417(8) |
| Tl–O40 | 2.799(4) | C21–N21 | 1.315(9) | C51–N51 | 1.320(9) |
| Tl–O50$^{i[a]}$ | 2.599(5) | C21–S20 | 1.682(7) | C51–S50 | 1.659(8) |

[a] Symmetry operation used to generate equivalent atoms: i, $x$, $3/2 - y$, $z - 1/2$.

triangular bipyramid taking into account a stereochemically active 6s lone pair of the $Tl^+$ ion as a fifth ligand. An analogous coordination geometry has been recently reported for $Pb^{2+}$ ions in a polymeric complex with the ligand $H_2L^1$.[27] The intermolecular Tl–O interaction is responsible for the formation of the 1D polymeric chain $[TlFe(L^2)_2]_\infty$ in the solid state (Figure S2.2b) and can be considered as a driving force for the separation of the anionic species $[Fe(L^2)_2]^-$ from the reaction mixture by means of the large cation $Tl^+$. Another striking feature of the complex is the great deviation of the $-C(S)-NEt_2$ parts from the ligand planes (Figure 2b). Such deviation prevents electron delocalization within aroylthiourea moieties, even within the *S,O* chelate ring surrounding $Tl^+$. This is in agreement with the moderate bathochromic shift of the $\nu_{C=O}$ band observed in the IR spectrum and provides an explanation for the lower degree of double bond character of the $C(S)-N_{amide}$ bonds compared to the adjacent C–N bonds.

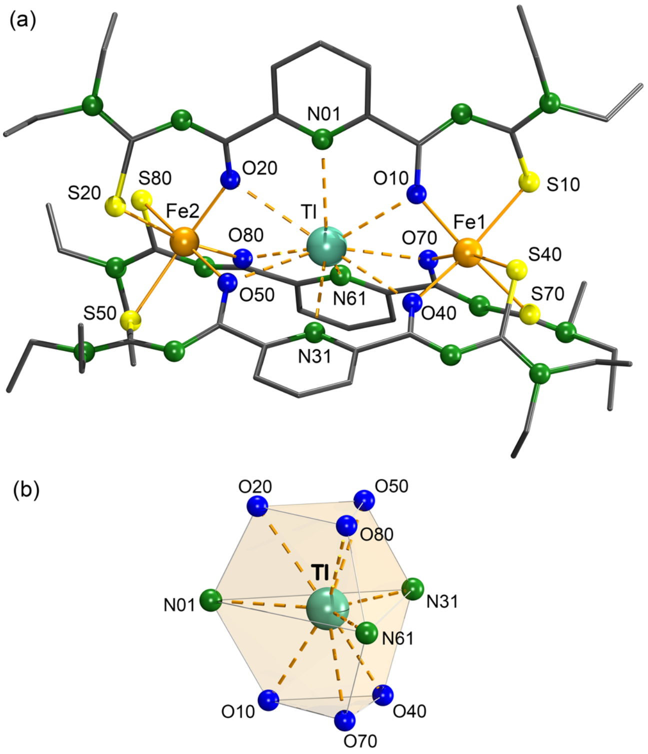


**Figure 3.** (a) Structure of the cationic Fe(III) {2}-metallacryptate $\{Tl\subset[Fe_2(L^2)_3]\}^+$. Hydrogen atoms are omitted for clarity. (b) Axially truncated trigonal bipyramidal coordination sphere surrounding the guest cation $Tl^+$.

The failed synthesis of the {2}-metallacryptand $[Fe(L^2)_3]$ indicates that the "hard" acid $Fe^{3+}$ favors a mixture of "borderline" and "hard" base donor sets (*N,N,N* and *O,N,N*) over a mixture of "soft" and "hard" base chelators (*S,O*). In order to direct $Fe^{3+}$ to the *S,O*-chelating aroylthiourea unit for coordination, reactions of $H_2L^2$ with mixtures of $Fe^{3+}$ and "harder" metal ions were carried out. In the above-mentioned reaction, $Tl^+$ was added only in a second step of the reaction and did not compete with the $Fe^{3+}$ ions for the favored pyridine nitrogen donors, and finally only acts as a "counterion". When $Tl^+$ is added together with the $Fe^{3+}$ ions to $H_2L^2$ before the addition of the supporting base, the reaction gives a completely different product (Scheme 2). The resulting ionic complex can be separated as $PF_6^-$ salt upon addition of $(n\text{-}Bu_4N)(PF_6)$ with a yield of 56%. The presence of the counteranion is verified by a strong band in the IR spectrum of the isolated solid at 839 $cm^{-1}$, which is characteristic of the $\nu_{P-F}$ vibrations.[42] The disappearance of the $\nu_{NH}$ band in the region above 3100 $cm^{-1}$ and the strong bathochromic shift of the $\nu_{C=O}$ band by about 170 $cm^{-1}$ prove the deprotonation of the ligand and the formation of *S,O* chelates with extended $\pi$-systems. This information is a positive sign concerning the formation of the expected {2}-ironcryptand $[Fe_2(L^2)_3]$. An X-ray structure analysis of the resulting complex confirms these conclusions by revealing a host–guest compound with the composition of $\{Tl\subset[Fe_2(L^2)_3]\}(PF_6)$ (**8a**$(PF_6)$). The cationic {2}-ironcryptate presented in Figure 3a is most probably not simply generated by the capture of the guest $Tl^+$ ion into the void of the {2}-ironcryptand $[Fe_2(L^2)_3]$ composed of two $Fe^{3+}$ ions and three pentadentate deprotonated ligands $(L^2)^{2-}$. The $Tl^+$ ion plays a vital role in the formation of the {2}-ironcryptand by acting as a template. In particular, the $Tl^+$ ion occupies the central coordination positions of the $\{L^2\}^{2-}$ ligands and, thus, interferes with the potential formation of *N,N,N* or *N,N,O* coordination of the $Fe^{3+}$ ions as is observed in $[TlFe(L^2)_2]_\infty$. In the $\{Tl\subset[Fe_2(L^2)_3]\}^+$ ion, each Fe atom is coordinated in a distorted octahedral environment with a facial arrangement of the sulfur atoms as found before for the tris-complexes of In(III) and Fe(III) with the ligand $H_2L^1$. The Fe–S bond lengths in the range 2.368(4)–2.451(9) Å are in good agreement with those found in $[Fe_2(L^1)_3]$, while the Fe–O bonds range between 2.003(3) Å and 2.045(3) Å and are slightly longer than the corresponding bonds in $[Fe_2(L^1)_3]$. The elongation of the Fe–O bonds provides more space and more electron density for the $Tl^+$ ion in the central void. In the final arrangement, the three metal ions show an almost linear arrangement. The requirement of a negative charge to capture the guest cation causes a partial location of $\pi$-electron density on the oxygen atoms and a less degree of delocalization in the chelate rings, which is pointed out by the clear distinction

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between the adjacent C(O)−$N_{amide}$ and C(S)−$N_{amide}$ bond lengths (Table S2.3). Adopting an axially truncated trigonal bipyramidal geometry, the guest cation is nine-coordinate with six oxygen donors and three pyridine nitrogen donors forming the mutual base of the bipyramid (Figure 3b).

This coordination mode is hitherto unknown for $Tl^+$ and very rare for other hard monovalent metal ions such as alkali metal ions, where only a few examples of potassium-containing compounds have been reported.[43−45] This lack of information motivated us to undertake ongoing studies with the alkali metal ions $Li^+$, $Na^+$, $K^+$, $Rb^+$, and $Cs^+$ instead of $Tl^+$.

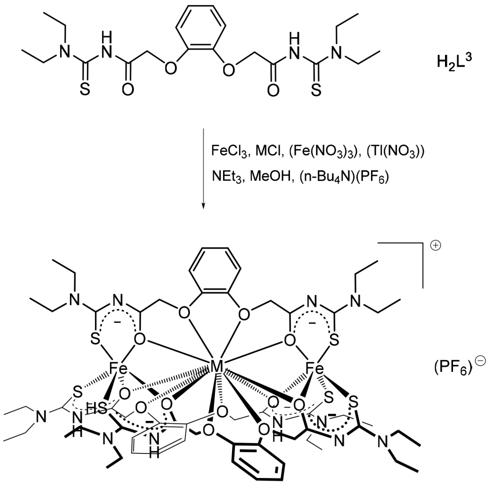
Applying the same synthetic route as described for the thallium product (one-pot reactions between $FeCl_3$, alkali metal chlorides, $H_2L^2$, and $NEt_3$ in methanol with subsequent addition of $(n\text{-}Bu_4N)(PF_6)$) gave pure products, which precipitated directly from the reaction mixtures. The proposed compositions $\{M\subset[Fe_2(L^2)_3]\}(PF_6)$ (M = $Rb^+$ (**8b**), $K^+$ (**8c**), or $Na^+$ (**8d**)) of the isolated solids are supported by elemental analyses, IR spectroscopy, and X-ray structural analyses. No unusual features were found in the IR spectra or in the molecular structures of the products The structures of these compounds and selected bond lengths and angles are given in Figure S2.4 and Table S2.4. Like the $Tl^+$ ions in compound **8a**, the alkali metal ions in compounds **8b**−**8d** possess coordination environments, which are best described by axially truncated triangular bipyramids, which consist of three pyridine nitrogen atoms being located at the vertices of the mutual triangular base and six carbonyl oxygen atoms occupying the remaining vertices of the two truncated triangular pyramids. The $ESI^+$ mass spectra of the inclusion compounds with alkali metal ions strongly support the existence of the cationic complex species by the presence of peaks of the fragments $[\{M\subset[Fe_2(L^2)_3]\}]^+$ (M = $Na^+$, $K^+$, or $Rb^+$). Meanwhile, only the peak of the fragment $[\{K\subset[Fe_2(L^2)_3]\}]^+$, which results from the exchange of the guest cation with $K^+$ of the MS matrix, appears in the mass spectrum of **8a**.

It should be mentioned that inclusion complexes of the type **8** could not be isolated with $Li^+$ or $Cs^+$ guest ions. This might be explained by the radii of these ions. While the radii of $Na^+$, $K^+$, $Rb^+$, and $Tl^+$ are all in the range from 1.18 to 1.61 Å,[46] the size of the $Li^+$ ion (0.92 Å) seems to be too small to be stabilized in such a 9-coordinate environment. On the other hand, the cavity formed by the {2}-ironcryptate with three $\{L^2\}^{2-}$ ligands seems to be too small to host the large $Cs^+$ ions (1.74 Å). This fact poses the question for the behavior of similar compounds with the ether-spaced ligand $H_2L^3$, which possesses two oxygen donor atoms instead of the central pyridine nitrogen atom of $H_2L^2$. Thus, it should be able to establish compounds with larger central cavities, provided it also undergoes the expected, template-directed formation of {2}-ironcryptands.

One-pot reactions of the ligand $H_2L^3$ with mixtures of $FeCl_3$ and MCl (M = $Cs^+$, $Rb^+$, $K^+$) or $Fe(NO_3)_3$ and $TlNO_3$ in MeOH result in dark-red solutions. The addition of $Et_3N$ and subsequent workup with $(n\text{-}Bu_4N)(PF_6)$ give dark-red solids, which are readily soluble in organic solvents such as $CH_2Cl_2$ or chloroform (Scheme 3).

In the IR spectra of products, there are no absorptions in the region above 3100 $cm^{-1}$ corresponding to $\nu_{NH}$ stretches, which can be found in the spectrum of the uncoordinated ligand. This is a strong hint for the existence of the doubly deprotonated form $(L^3)^{2-}$ of the ligand. The formation of chelate rings after the coordination, which is normally accompanied by a large

**Scheme 3. Synthesis of the $\{M\subset[Fe_2(L^3)_3]\}(PF_6)$ Complexes**



9a: M = K, 9b: M = Rb, 9c: M = Cs, 9d: M = Tl

delocalization of π-electrons, is proved by bathochromic shifts of the $\nu_{C=O}$ bands from 1660 $cm^{-1}$ in $H_2L^3$ to the region around 1560 $cm^{-1}$. These shifts are remarkable, however not as high as observed in other benzoylthiourea chelates, where these bands usually appear between 1400 and 1500 $cm^{-1}$. An additional strong absorption band around 840 $cm^{-1}$ is assigned to the $\nu_{P-F}$ stretches. The existence of $\{M\subset[Fe_2(L^3)_3]\}^+$ (**9**) species (M = $Cs^+$, $Rb^+$, $K^+$, or $Tl^+$) are also proven by the detection of corresponding fragments in the $ESI^+$ mass spectra of the complexes. These observations and the elemental analyses strongly suggest a general composition of $\{M\subset[Fe_2(L^3)_3]\}(PF_6)$ (M = $Cs^+$, $Rb^+$, $K^+$, or $Tl^+$) of the metal−ligand assemblies. Single crystals suitable for X-ray crystallography were produced from slow evaporation of $CH_2Cl_2$/MeOH solutions.

As a representative for the cationic host−guest complexes $\{M\subset[Fe_2(L^3)_3]\}^+$, the structure of the corresponding potassium compound is shown in Figure 4a. The structures of the $Rb^+$, $Cs^+$, and $Tl^+$ inclusion compounds are virtually identical and shall, thus, not be shown in extra figures. Selected bonding parameters of all compounds, however, are summarized in Table 2. A structural analysis of the $\{M\subset[Fe_2(L^3)_3]\}^+$ cations shows $C_3$ symmetry for the {2}-metallacryptates. The three metal ions are situated on a crystallographic 3-fold axis (Figure 4b). As expected, the metallacryptand "$[Fe_2(L^3)_3]$" is composed of two Fe(III) ions linked through three doubly deprotonated ligands $(L^3)^{2-}$. As a consequence, each $Fe^{3+}$ ion is octahedrally coordinated to three *S*,*O*-chelating aroylthioureato moieties with facial arrangement of the sulfur atoms. In analogy to the Fe(III) metallacryptands derived from $H_2L^2$, the resulting Fe(III) {2}-metallacryptand is capable to encapsulate a hard monovalent cation in the central cavity. Alkaline metal ions like $K^+$, $Rb^+$, and $Cs^+$ or $Tl^+$ ions are 12-coordinate by six carbonyl and six ether-oxygen donors.

Despite the fact that the Fe−O and Fe−S bond lengths (Table 2) are in the same ranges for those in Fe(III) triscomplexes discussed in the preceding parts, the observed planarity of chelate rings containing $\{L^3\}^{2-}$ ligands is in direct contrast to the considerable distortions observed in the related complexes with $\{L^1\}^{2-}$ or $\{L^2\}^{2-}$. This significant difference arises from the higher flexibility of the backbone of the ligand $H_2L^3$. In $\{L^3\}^{2-}$, free rotation of two aroylthiourea arms around

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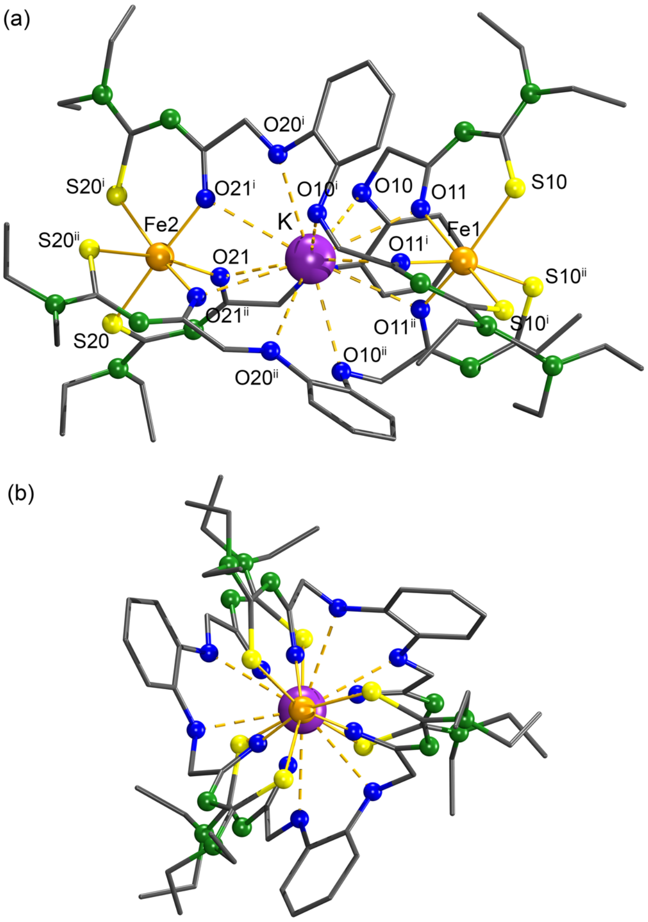

**Figure 4.** (a) Structure of the cationic Fe(III) {2}-metallacryptate $\{K{\subset}[Fe_2(L^3)_3]\}^+$. Hydrogen atoms are omitted for clarity. Symmetry operations used to generate equivalent atoms: i, $-y$, $x - y$, $z$; ii, $-x + y$, $-x$, $z$. (b) View along the crystallographic 3-fold axis.

the O−$CH_2$ bonds, which is reflected by the torsion angles $C_{ar}$−O−$CH_2$−C(O) (Table 2), is responsible for providing an optimal coordination environment for metal ions. On the other hand, in $\{L^1\}^{2-}$ and $\{L^2\}^{2-}$, conjugation of two aroylthiourea moieties with the aromatic spacers prevents such a free rotation. Thus, the adaptation of the ligand skeletons for chelating the metal ions is exclusively done by deviations of donor atoms from the chelate planes, in other words by the distortion of chelate rings.

The utilization of $Fe^{3+}$ ions in the metallamacrocycles produced compounds with a redox behavior, which makes them interesting for electrochemical studies. Thus, cyclic voltammetry measurements of the representative compounds $[Fe_2(L^1)_3]$, $\{K{\subset}[Fe_2(L^2)_3]\}(PF_6)$, and $\{K{\subset}[Fe_2(L^3)_3]\}(PF_6)$ were undertaken in dry DMF under an atmosphere of dry argon. Cyclic voltammetric parameters of electron transfer processes are summarized in Table 3. The voltammograms display two consecutive one-electron transfer processes corresponding to the quasi-reversible, stepwise reduction of the two iron ions (Scheme 4).

**Table 3. Cyclic Voltammetric Parameters of Consecutive One-Electron Transfer Processes of the Iron(III) Metallacryptates under Study**

| complex | $E_{pc}$ (V) | $E_{pa}$ (V) | $E°_1{}'$ (V) | $E°_2{}'$ (V) |
|---|---|---|---|---|
| $[Fe_2(L^1)_3]$ | −0.965 | −0.756 | −0.797 | −0.922 |
| $\{K{\subset}[Fe_2(L^2)_3]\}(PF_6)$ | −0.782 | −0.579 | −0.616 | −0.737 |
| $\{K{\subset}[Fe_2(L^3)_3]\}(PF_6)$ | −0.832 | −0.663 | | |

Particularly, the cryptand-like complex $[Fe_2(L^1)_3]$ shows two quasi-reversible reductions at −0.797 V ($\Delta E_p$ = 82 mV) and −0.922 V ($\Delta E_p$ = 86 mV) that correspond to one-electron transfer processes (Figure 5a). It is necessary to note that under the same conditions the $\Delta E_p$ value of the $Fc^+$/Fc couple is 74 mV. In the case of the metallacryptate $\{K{\subset}[Fe_2(L^2)_3]\}(PF_6)$, it undergoes two quasi-reversible one-electron reductions at −0.616 V ($\Delta E_p$ = 80 mV) and −0.737 V ($\Delta E_p$ = 82 mV) (Figure 5b). The $\Delta E_p$ values of the corresponding redox waves are comparable to that of the $Fc^+$/Fc couple ($\Delta E_p$ = 78 mV). In comparison with moderately resolved voltammograms of the compounds $[Fe_2(L^1)_3]$ and $\{K{\subset}[Fe_2(L^2)_3]\}(PF_6)$, the two peaks corresponding to the redox processes of the Fe(III) ions in $\{K{\subset}[Fe_2(L^3)_3]\}(PF_6)$ overlap and become indistinguishable (Figure 5c). Such low resolution of redox waves directly relates to structural features of the corresponding complexes. Specifically, since the separation of the two redox potentials strongly depends on the degree of interactions between the two redox centers of the intermediate mixed-valent compounds,[47,48] the partially separated features of signals in the voltammograms recorded for the complexes of $H_2L^1$ and $H_2L^2$ (Figures 5a and 5b) indicate slight delocalization of charge between the two iron ions. This can be caused by the conjugation of the chelating aroylthioureas with the aromatic spacers. In contrast, the aliphatic O−$CH_2$ bonds prevent a potential conjugation in the backbone of $(L^3)^{2-}$ ligands and, hence, produce electronic isolation of two iron ions, which is responsible for the poor resolution of the related redox waves (Figure 5c).

## ■ CONCLUSIONS

A series of oligonuclear systems has been developed for three aroylbis(*N*,*N*-dialkylthiourea) ligands. Reaction of $H_2L^1$ with $Fe^{3+}$ ions results in the binuclear complex $[Fe_2(L^1)_3]$ with a cryptand-like structure, while one-pot reactions of $H_2L^2$ or $H_2L^3$ with mixtures of Fe(III) ions and monovalent, "hard" ions such as $Cs^+$, $Rb^+$, $K^+$, $Na^+$, or $Tl^+$ give rise to {2}-metallacryptates. These host−guest assemblies are afforded by the encapsulation of one guest monocation $M^+$ in the central void of the {2}-metallacryptands $\{Fe_2(L)_3\}$ (L = $L^2$ or $L^3$),

**Table 2. Selected Bond Lengths (Å) and Torsion Angles (deg) in $\{M{\subset}[Fe_2(L^3)_3]\}(PF_6)$ Complexes**

| M | Fe−O | Fe−S | M−O | torsion angle[a] |
|---|---|---|---|---|
| $Cs^+$ | 1.998(3)/2.011(3) | 2.405(5)/2.413(6) | 3.182(3)−3.251(3) | −179.00(5)/−73.44(9) |
| $Rb^+$ | 2.009(4)/2.014(4) | 2.404(2)/2.415(8) | 3.097(4)−3.185(4) | −175.22(6)/−72.64(2) |
| $Tl^+$ | 2.008(4)/2.012(4) | 2.405(7)/2.416(5) | 3.105(4)−3.219(4) | 176.75(2)/71.90(1) |
| $K^+$ | 2.006(4)/2.007(4) | 2.402(4)/2.415(8) | 3.030(4)−3.155(4) | −173.10(2)/−72.28(7) |

[a] Torsion angle ∠{$C_{ar}$−O−$CH_2$−C(O)}.

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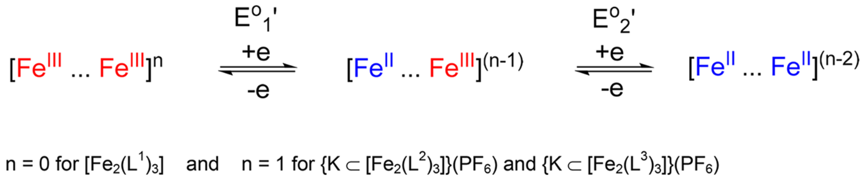
**Scheme 4. Stepwise Reduction of Fe(III) Centers in the Fe(III) Metallacryptands under Study**[a]



[a] Guest cations and ligands are excluded for simplification.

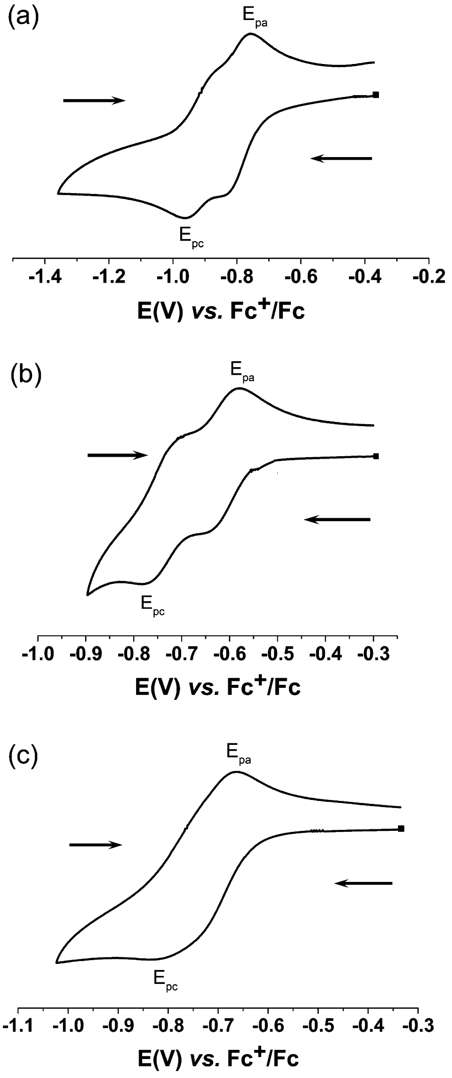


**Figure 5.** Cyclic voltammograms of the complexes (2 mM) in 0.15 M ($n$-$Bu_4N$)($PF_6$)−DMF at a scan rate of 150 mV/s: (a) [$Fe_2(L^1)_3$], (b) {K⊂[$Fe_2(L^2)_3$]}($PF_6$), and (c) {K⊂[$Fe_2(L^3)_3$]}($PF_6$).

which are formed by the coordination of two Fe(III) ions with three aroylbis(thioureato) dianions $(L^2)^{2-}$ or $(L^3)^{2-}$. The failure of all attempts to prepare the {2}-metallacryptand [$Fe_2(L^2)_3$] in the absence of guest cations apparently demonstrates that the metal−ligand self-assembly is driven by the template effect of the guest monocations. Structural characterization of the obtained oligonuclear assemblies and studies on electrochemical properties of three representative complexes expose considerable influences of the coordination capacity and flexibility of the ligand systems on the resulting coordination systems.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b01909.

Spectroscopic data, ellipsoid representations of the oligonuclear complexes, and structural parameters (PDF)

### Accession Codes

CCDC 1545457, 1545460−1545463, and 1545465−1545469 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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